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### (54) Method for masking a portion of metal to be carburized or nitrided

(57) The object of the present invention is to provide a method for masking a portion of a material to be carburized or nitrided in partial carburizing and nitriding treatment, in which the powder for prevention of carburizing or nitriding is coated on metal materials, only the

portion to be masked is heated by laser beam, so that the powder is fused and bonded to form a masking film on said portion alone.

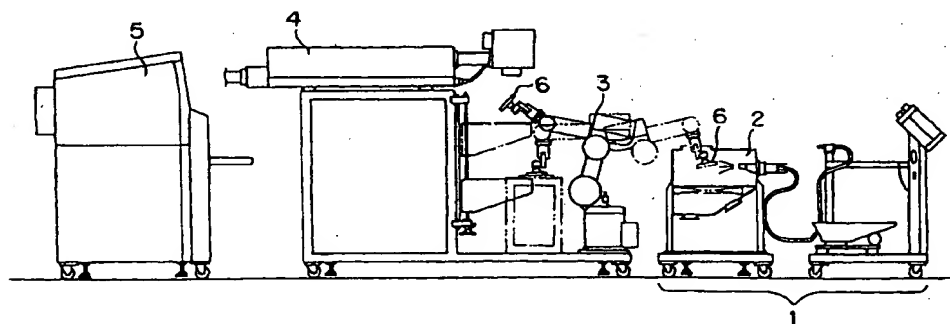


Fig. 1

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nitrided, which comprises coating the powder for prevention of carburizing or nitriding over a region including at least said portion to be prevented from being carburized and nitrided, heating only said portion by laser beam, thereby fusing and bonding the powder to only the portion to be prevented from being carburized and nitrided.

In particular, the present invention relates to the method for masking carburizing and nitriding in which a powder comprising as essential components the substance having a carburizing or nitriding preventing action and the thermally fusible resin to be thermally decomposed under carburizing or nitriding conditions is used as the powder for prevention of carburizing and nitriding.

According to the present invention, the powder for prevention of carburizing and nitriding is applied by a coating method such as an electrostatic coating to the whole of a material treated or to a region including at least the portion to be prevented from being carburized and nitrided, and then only said portion is heated by laser irradiation to a temperature higher than the fusing temperature, and said powder is fused and bonded to just said portion. Hence, regardless of the shape and surface conditions of the base material, said powder can be allowed to adhere easily and accurately to only the portion to be prevented from being carburized and nitrided. The heating temperature should be set higher than the fusing temperature of the fusible components in the powder, and usually the powder is heated at about 120 to 350°C. The powder on the site not irradiated with the laser, i.e. the site not requiring carburizing and nitriding preventing treatment, is neither fused and bonded onto the material treated and can thus be removed by e.g. air spraying after laser irradiation.

The heating means are desirably those capable of heating only the target portion reliably and accurately regardless of whether the shape of the material treated has a curved surface or unevenness or whether the site thereof to be prevented from being carburized and nitrided has a complex or fine pattern. As such heating means, a laser beam heating method is used in the present invention.

After the material to be treated is coated with a powder for prevention of carburizing and nitriding, this heating means is used to strictly heat only the portion to be prevented from being carburized and nitrided whereby the powder for prevention of carburizing and nitriding can be allowed to adhere to only the heated site easily and reliably. After the powder is fused and bonded onto the given portion in this manner, the material is subjected to carburizing and nitriding treatment where a temperature of 500 to 1000°C is usually used, so before this temperature is reached, the resin in said powder is thermally decomposed and disappears, and only the substance having a carburizing and nitriding preventing action remains to form a carburizing and nitriding preventing film, thus preventing the portion

from being carburized and nitrided.

The laser beam heating method used in the present invention is carried out preferably using a scanning type beam irradiation apparatus equipped with a scanning head for scanning depending on a pattern memorized in a computer to emit laser rays to only a portion requiring heating.

For a pattern to be irradiated with the laser beam, the laser emitting head may be moved by the computer, or while the emitting head is fixed, the material treated may be moved, and in either case, it is preferable to trace the pattern by automatic control.

The width of the emitted laser beam is selected depending on the size and accuracy of the portion to be subjected to carburizing and nitriding preventing treatment. To strictly heat only the portion to be prevented from being carburized and nitrided, the irradiation apparatus is preferably that capable of adjusting beam width to 1.0 mm, preferably 0.1 mm. For laser output, the size of the laser is selected such that it can rapidly heat the desired portion of the material treated.

The computer-controlled laser generating apparatus satisfying these requirements may be those commercially available, including e.g. scanning type laser maker apparatus ML-4140 C (manufactured by Miyachi Technos K.K.).

The specific method of permitting the powder for prevention of carburizing and nitriding adhere to the material treated is not particularly limited, and it is possible to suitably modify and employ conventional methods such as fluidization dip method, spray method, electrostatic adhesion method etc.

FIG. 1 shows a preferable example of an automatic apparatus capable of laser beam heating and applying the powder for prevention of carburizing and nitriding. The method for prevention of carburizing and nitriding according to the present invention will be described by reference to this drawing.

Test specimen (6) requiring partial prevention of carburizing and nitriding is transferred by 6-axis robot (3) to powder coating booth (2) where the powder for prevention of carburizing and nitriding is allowed to adhere by electrostatic coating to the whole of the test specimen. This test specimen is transferred by the 6-axis robot to the laser irradiation position in YAG laser marker (4), and only the portion requiring prevention of carburizing and nitriding is irradiated with the laser whereby the powder for prevention of carburizing and nitriding is fused and bonded to only that portion of the test specimen. For laser irradiation, the X- and Y-axes for laser irradiation can be controlled by laser maker controller (5), and the Z-axis can be controlled by the 6-axis robot. Thereafter, the robot transfers the test specimen to the coating booth, and the powder not fusion-bonded is scattered by air blow.

The substance having a carburizing and nitriding preventing action, which constitutes the powder for prevention of carburizing and nitriding in the present inven-

acryl type resin. If the thermosetting resin is used, it is preferable to select a hardening agent to show hardening reaction by releasing a blocking agent after the main agent is thermally plasticized by blocking a cross-reactive functional group.

The amount of the thermally fusible resin in the powder for prevention of carburizing and nitriding according to the present invention is preferably in the range of 20 to 80% by weight, more preferably 40 to 60% by weight, and if the amount of the incorporated resin is deficient, the powder tends to be difficult in the following method to be fused and bonded to the portion to be prevented from being carburized and nitrided, whereas given a large amount of the incorporated resin, the absolute amount of the boron-based inorganic compound or boron oxide-based amorphous substance becomes deficient, thus making it difficult to form a close masking film, and in either case, none of satisfactory carburizing and nitriding preventing effects may be obtained.

However, if a powder containing a suitable amount of the boron-based inorganic compound or boron oxide-based amorphous substance and the thermally fusible resin is used, the powder which adhered to the surface of the metal to be treated is uniformly fused and bonded onto the heated portion (i.e. the portion to be prevented from being carburized and nitrided) of the material treated by virtue of the adhesiveness of the thermally fusible resin accompanying its thermal plasticization, and when it is exposed to a carburizing and nitriding atmosphere at 400°C or more, the thermally fusible resin disappears by thermal decomposition, and simultaneously the sufficient amount of the boron oxide-based amorphous substance in the powder is molten or fused and bonded onto the material thereby forming a close masking film thereon with good adhesion in the absence of pinhole defects etc., thus bringing about reliable prevention of carburizing and nitriding.

Although the essential constitutional components in the powder for prevention of carburizing and nitriding according to the present invention are the 2 components described above. As other components, water glass, frit, low-melting glass or metal powder such as tin, aluminum, zinc etc. or disrupted metal foil etc. can be added in suitable amounts to improve the carburizing and nitriding preventing effects. Additional materials such as titanium oxide, iron oxide, zinc oxide, talk, calcium carbonate, mica, silica (molten silica, aerosol etc.), alumina, magnesium, silicon carbide, fly ash, graphite, silicic acid, kaolinite, clay etc. are added in small amounts to improve the adhesive properties or denseness of the carburizing and nitriding preventing film which is fusion-bonded on the material treated, or to prevent the fluidity (sagging properties) of the carburizing and nitriding preventing coating at the time of carburizing or nitriding treatment.

In addition, the powder for prevention of carburizing and nitriding is preferably colored with various pigments

to improve degrees of absorption of the laser. Selection of the color depends on the thermal absorption of laser rays, and colors such as green, red etc. are relatively desirable. To improve degrees of absorption, colloidal graphite etc. may be applied onto the surface of the material treated.

The powder for prevention of carburizing and nitriding according to the present invention is a mixture of the above constitutional components, and the process for preparation thereof is not limited at all, and for example, the boron oxide-based amorphous substance in a powder form and the thermally fusible resin in a powder form and if necessary other auxiliary additive may be blended and uniformly mixed with one another. Alternatively, in a preferable process, the thermally fusible resin is heated and softened, and then the powdery boron oxide-based amorphous substance and other powdery auxiliary additives are uniformly dispersed in it, and the mixture is cooled, solidified and disrupted so that the powder with uniform components can be easily obtained without separation of individual constitutional components from each other. In a similar preferable process, the thermally fusible resin is dissolved in suitable solvent, and then the powdery boron oxide-based amorphous substance and other powdery auxiliary additives are uniformly mixed with it, followed by spray-drying.

To permit the powder for prevention of carburizing and nitriding to adhere evenly and uniformly to the portion to be prevented from being carburized and nitrided, the diameter of the powder is preferably regulated in the range of 10 to 250  $\mu\text{m}$  in average, more preferably 50 to 200  $\mu\text{m}$ . If the powder is too coarse, there is a tendency for an uniform carburizing and nitriding preventing film to be hardly formed, whereas it is too fine, there is a tendency for a thick carburizing and nitriding preventing film to be hardly formed, making it difficult to achieve satisfactory carburizing and nitriding preventing effects.

The content of the boron-based inorganic compound or boron oxide-based amorphous substance having a carburizing or nitriding preventing action in this powder for prevention of carburizing or nitriding is in the range of 20 to 80% by weight, preferably 40 to 60% by weight in terms of anhydrides thereof, and the preferable content of the thermally fusible resin to be thermally decomposed under carburizing or nitriding conditions is in the range of 20 to 80% by weight, preferably 40 to 60% by weight.

A particularly preferable example of such a boron-based inorganic compound or boron oxide-based amorphous substance is that with a water content of 10% by weight or less, more preferably 5% by weight, and a preferable example of thermally fusible resin is one member selected from polyolefin type resin, polyester type resin and acryl type resin or a mixture thereof.

The material to be treated to which the present invention is applied includes various metal materials whose surface hardening is carried out by partial carbu-

8. A method for masking according to claim 5 or 6, wherein the boron oxide-based amorphous substance consists of 60 to 90% by weight  $B_2O_3$  and 40 to 10% by weight  $SiO_2$ , and the water content thereof is 10% by weight or less.

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9. A method for masking according to any one of claims 4 to 8, wherein the thermally fusible resin is at least one kind of resin selected from

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polyolefins, polyesters and acrylic resins.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 10 5629

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 419 675 A (K.K. NARD KENKYUSHO) 3 April 1991		C23C8/04
A	DE 19 51 926 A (STATNI VYZKUMNY USTAV MATERIALU) 22 April 1971		
A	FR 1 243 555 A (ZAHNRADFABRIK FRIEDRICHSHAFEN) 16 January 1961		
A	US 3 661 820 A (ROBERT W. FOREMAN) 9 May 1972		
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 387 (E-566), 17 December 1987 & JP 62 154524 A (HITACHI LTD), 9 July 1987, * abstract *		
A	EP 0 377 444 A (TAMGLASS OY) 11 July 1990		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C23C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>10 June 1998</b>	Examiner <b>Elsen, D</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)

## Description

The present invention relates to a method for masking, carburizing and nitriding, and in particular to a method for masking carburizing and nitriding by means of a powder for prevention of carburizing and nitriding so that a portion of a metallic part such as steel etc. is hardened by carburizing and nitriding while the toughness of the other portion remained in non-carburized or non-nitrided states is maintained.

In metallic machine parts such as cams, shafts, pistons, pins or various gears and cutting tools used for automobiles, ships etc., the parts as a whole require toughness, while the parts undergoing friction require high-level wear resistance. As a method of obtaining such machine parts having both toughness and wear resistance, there is a method in which a tough steel material is used and only the portion thereof requiring wear resistance is hardened by subjecting it to carburizing and nitriding treatment, and in this case, the other portion not to be hardened is prevented by masking from being carburized and nitrided, thus keeping its toughness.

Although this type of conventionally used masking material includes copper plating or tin plating, the plating operation for masking is complicated and cumbersome, so coating-type masking materials for forming a gas barrier film were developed recently and came to be distributed rapidly. That is, the coating-type masking materials are those containing chemical powder (e.g. borax and borosilic acid or tin powder) having a carburizing and nitriding preventing action added to a small amount of resin and solvent, and this coating is applied onto a specific portion of a steel material before thermal treatment for carburizing and nitriding. Then, the material is introduced into a furnace charged with a carburizing and nitriding agent or in an atmosphere of carburizing and nitriding gas and then heated at 300 to 1000°C whereby the resin in the coating is thermally decomposed and disappears, while the carburizing and nitriding preventing components in the coating are baked on the surface of the steel material to form a carburizing and nitriding preventing film by which the material is prevented from contacting with the carburizing and nitriding components, thus preventing said coated portion from being carburized and nitrided. In this case, if an uneven coating, pinhole defects etc. are present on the carburizing and nitriding preventing film, the object of preventing carburizing and nitriding cannot be achieved, so it is essential to form a defect-free and uniform carburizing and nitriding preventing film.

However, this coating has a less amount of incorporated resin components working as vehicle components (because a larger amount leads to significant discharge of its decomposed gas, and the baking of the carburizing and nitriding preventing components is thus prevented), so its flow-out is inadequate, and it is necessary that the coating should be diluted with sol-

vent and applied repeatedly in order to form a uniform film. Accordingly, this requires careful operation and much labor using brush etc.

As a method for masking of carburizing and nitriding in which reliable carburizing and nitriding effects can be obtained regardless of whether the surface of a substrate treated is flat, curved or uneven, the present inventors disclosed, in Japanese Patent Application No. 91436/96, a method wherein a powder for prevention of carburizing and nitriding containing as essential components a boron-based inorganic compound having a carburizing or nitriding preventing action and thermally fusible resin to be thermally decomposed under carburizing and nitriding conditions is fused and bonded onto the portion of a treated metal to be prevented from being carburized and nitrided. By this method for carburizing and nitriding preventing treatment, a thick film excellent in carburizing and nitriding preventing effects could be formed uniformly using the simple means regardless of the shape and surface conditions of a base material to be treated.

In the above method for masking of carburizing and nitriding by use of the carburizing and nitriding preventing agent comprising the substance having a carburizing and nitriding preventing action and thermally fusible resin in the carburizing and nitriding treatment, the above carburizing and nitriding preventing agent should accurately and completely be applied without any gap to the portion whose carburizing and nitriding are intended to be prevented. For such application, only the portion to be subjected to carburizing and nitriding treatment should be heated accurately and adequately at a temperature not lower than the fusing temperature of the thermally fusible resin.

The object of the present invention is to provide a method for accurately carburizing and nitriding a portion to be subjected to carburizing and nitriding treatment by permitting a carburizing and nitriding preventing agent to be fused and bonded accurately to only the portion to be masked from being carburized and nitrided.

The above problem has been solved by a method for masking from carburizing and nitriding which is characterized in that only the portion to be prevented from carburizing or nitriding is heated selectively by a laser beam.

The present invention relates to a method for masking a portion of a metal material to be carburized or nitrided, which comprises coating a powder for prevention of carburizing or nitriding over a region including at least said portion to be prevented from being carburized and nitrided, heating only said portion by laser beam, thereby fusing and bonding the powder to only the portion to be prevented from being carburized and nitrided.

FIG. 1 shows a side view of one embodiment for carrying out the carburizing and nitriding preventing treatment of the present invention.

The present invention relates to a method for masking a portion of a metal material to be carburized or

tion, is preferably a boron-based inorganic compound or boron oxide-based amorphous substance. Such a boron-based inorganic compound or boron oxide-based amorphous substance is softened under heating conditions carburizing and nitriding treatment (usually 300 to 1000°C) and almost simultaneously with combustion by thermal decomposition of the aforementioned fusible resin, forms a close carburizing and nitriding preventing film, thereby demonstrating carburizing and nitriding preventing functions. As such compounds, boron-based inorganic compounds are selected and these can be baked on the surface of a base material at a temperature of 450°C or more to form a close carburizing and nitriding preventing film thereon.

The boron-based inorganic compounds include e.g. borax, boron oxide, borosilicic acid, phenyl boric acid etc. Boron oxide is particularly preferable.

The boron oxide-based amorphous substance used in the present invention is an amorphous substance comprising boron oxide  $B_2O_3$  and optionally other inorganic materials.

The preferable amorphous substance includes boron oxide-silicon oxide, boron oxide-silicon oxide-clay, boron oxide-silicon oxide-alumina, etc.

In the amorphous substance of boron oxide-silicon oxide,  $B_2O_3 : SiO_2$  is 65 to 95 : 35 to 5, preferably 70 to 90 : 30 to 10 (ratio by weight).

The boron-based inorganic compound or boron oxide-based amorphous substance is preferably that with a water content of 10% or less, more preferably 5% or less. If the water content in the boron-based inorganic compound or boron oxide-based amorphous substance is too high whether water is that of adhesion or of crystallization, evaporation of the water may cause pinhole defects etc. to be formed in the resulting masking film for preventing carburizing and nitriding, so that a reliable carburizing and nitriding preventing film is hardly formed or the carburizing and nitriding preventing film may not be formed at all.

To form the masking film having a thickness necessary and adequate for carburizing and nitriding prevention, the content of the boron-based inorganic compound or boron oxide-based amorphous substance in said powder is set preferably in the range of 20 to 80% by weight in terms of anhydrides thereof, and if its content is deficient, the carburizing and nitriding preventing film may become thin and uneven, and pinhole defects may occur after decomposition and combustion of the resin, making it difficult to achieve reliable carburizing and nitriding preventing effects. In contrast, if its content is too high, the absolute amount of the resin is made relatively deficient, and said powder may not adequately adhere to the portion to be prevented from being carburized and nitrided, so adhesion of the masking film formed at the time of carburizing and nitriding treatment is worsened, making it difficult to achieve reliable carburizing and nitriding preventing effects.

On the other hand, the characteristics of the ther-

mally fusible resin are that it acts as an adhesive component for permitting the powder for prevention of carburizing and nitriding to adhere to the portion to be prevented from being carburized and nitrided and that it is thermally decomposed to disappear under the carburizing and nitriding preventing treatment. That is, it is necessary to permit said powder to adhere to the portion to be prevented from carburized and nitrided; in the present invention, the adhesion of said powder to the portion to be prevented from being carburized and nitrided can be easily effected by incorporation of a predetermined amount of the thermal fusible resin as an essential component into said boron-based inorganic compound or boron oxide-based amorphous substance. As the thermally fusible resin, thermoplastic resin and thermosetting resin can be used, and these can easily adhere to the portion to be prevented from being carburized and nitrided because the thermoplastic resin is rendered softened and molten by heating and the thermosetting resin is rendered plasticized and fusible prior to hardening reaction.

Accordingly, the first characteristic of this thermally fusible resin is that it is rendered softened and molten by heating or plasticized and fused and bonded prior to thermal hardening reaction. It is desired to select the resin which is thermally fused and bonded to the material preferably at a temperature of 350°C or less, more preferably about 300°C or less. In the method described below, however, it is hard to permit the resin thermally fused and bonded at too high temperature, e.g. about 350°C or more, to reliably adhere to the portion to be prevented from carburized and nitrided, making it often difficult to achieve satisfactory carburizing and nitriding preventing effects.

The second characteristic of the fusible resin is that after the powder for prevention of carburizing and nitriding is allowed to adhere to the portion to be prevented from carburized and nitrided and before the carburizing and nitriding treatment is conducted, the resin should be thermally decomposed to disappear so as not to impair formation of a masking film consisting exclusively of the boron-based inorganic compound or boron oxide-based amorphous substance. Thus, it is desired to select the resin thermally decomposed to disappear preferably in the range of 400 to 600°C. This is because the resin which is thermally decomposed at too high temperature e.g. 700°C or more will undergo thermal decomposition during carburizing and nitriding to generate pinhole defects in the resulting carburizing and nitriding preventing film, making it difficult to achieve reliable carburizing and nitriding preventing effects.

As thermally decomposable resin satisfying these required characteristics, mention can be made of various kinds of resin, among which particularly preferably used are thermoplastic resins such as polyolefin type resin such as polyethylene, polypropylene etc., polyester type resin, and acryl type resin, and thermosetting resins such as thermosetting polyester type resin and

rizing and nitriding treatment, and the commonest materials are steel materials and alloy steels, and the present invention is applied to the portion to be prevented from, for example, carburizing and nitriding machine parts such as shafts and bearings or abrasive and grinding members so that the portion thereof undergoing strong friction and abrasion is hardened by carburizing and nitriding and the remaining portion is prevented from being carburized and nitrided, thus maintaining high toughness. In this manner, the portion to be prevented from being carburized and nitrided maintain its inherent toughness, whereas the non-adhered portion can be restrictively hardened by carburizing and nitriding treatment.

#### Examples

Hereinafter, the constitution and working effect of the present invention are described specifically by reference to Example and Comparative Example.

#### Example 1

As a test specimen for carburizing treatment, a cylindrical steel material of 22 mm diameter and 70 mm length was divided equally in the longitudinal direction to give semicylindrical specimens. This specimen was transferred to a coating booth (2) by the 6-axis robot shown in FIG. 1, and a powder for prevention of carburizing and nitriding (average particle diameter of 100  $\mu\text{m}$ ) consisting of 55% by weight boron oxide-silicon oxide type amorphous substance (i.e. 90% by weight boron oxide plus 10% by weight silicon oxide) and 45% by weight polyethylene powder was applied to the whole of the test specimen by electrostatic coating. Then, this test specimen was transferred to the laser irradiation position in YAG laser marker (4) by the 6-axis robot and the flat portion (bottom) of the semicylindrical specimen was irradiated with the laser under the control of a computer so as to draw a square pattern with a side of 5 mm. The test specimen after irradiation was transferred again to the coating booth (2) by the 6-axis robot, and the powder for prevention of carburizing and nitriding on the test specimen was blow away by air blow.

The powder for prevention of carburizing and nitriding was fusion-bonded on the test specimen to form a masking film at an accuracy of  $\pm 0.5$  mm.

Then, this test specimen was introduced into a carburizing heating furnace and subjected to carburizing treatment using gas type carburizing. After treatment, the test specimen was evaluated by observation under a microscope and its hardness was determined, and as a result, the hardness of only the portion whose wear characteristics were intended to be improved by carburizing treatment was accurately improved, and the portion protected with the powder for prevention of carburizing and nitriding was completely protected from the carburizing action.

#### Claims

1. A method for masking a portion of a metal material to be carburized or nitrided, which comprises coating the powder for prevention of carburizing or nitriding over a region including at least said portion to be prevented from being carburized and nitrided, heating only said portion by laser beam, thereby fusing and bonding the powder to only the portion to be prevented from being carburized and nitrided.
2. A method for masking according to claim 1, wherein the laser beam heating is effected by a laser beam emitted from an apparatus including a laser beam emitting unit and a computer for automatically controlling and driving the movement of a scanning head emitting a laser beam such that only the portion of the metal material to be prevented from being carburized and nitrided is irradiated with the laser beam.
3. A method for masking according to claim 2, wherein the scanning is controlled by a computer, in which the movement in the X- and Y-axial directions (horizontal biaxial directions with a right angle to each other) is conducted by the movement of the laser beam, and scanning in the vertical direction are conducted by a robot.
4. A method for masking according to any one of claims 1, 2 and 3, wherein the powder for prevention of carburizing or nitriding comprises as essential components a substance having a carburizing or nitriding preventing action and thermally fusible resins to be thermally decomposed under carburizing or nitriding conditions.
5. A method for masking according to claim 4, wherein the substance having a carburizing or nitriding preventing action is a boron-based inorganic compound or boron oxide-based amorphous substance.
6. A method for masking according to claim 4 or 5, wherein the content of the boron-based inorganic compound or boron oxide-based amorphous substance having a carburizing or nitriding preventing action in the powder for prevention of carburizing or nitriding is in the range of 20 to 80% by weight in terms of the content of anhydrides thereof, and the content of the thermally fusible resin to be thermally decomposed under carburizing or nitriding conditions is in the range of 20 to 80% by weight.
7. A method for masking according to claim 5 or 6, wherein the boron-based inorganic compound is a boron oxide with a water content of 10% by weight or less.



Fig. 1

